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¹ Preliminary communication.

² The paper will appear shortly in *Science, New York*, N. S., 1918. All the precautions mentioned in this account were carefully observed in the present investigation.

³ The methods previously used in studying the photosynthesis of aquatic plants are not as accurate as the one here described, nor do previous experiments afford the kind of data needed for our purpose. Cf. Blackman, F. F., and Smith, A. M., *Proc. Roy. Soc., London*, (B) **83**, 1911, (389).

⁴ All matching of shades was done under a 'Daylight' lamp, so that uniform conditions were assured throughout the experiments. Cf. *Science, New York*, N. S., **42**, 1915, (764). A clear space was left in the tube below the *Ulva* to facilitate comparison of colors. In any single experiment the buffer may be dispensed with by using as a standard the pink solution produced by the first exposure. The first exposure should be as short as is consistent with obtaining a definite standard. Experiments showed that the trace of alcoholic phenolphthalein had no injurious effect.

⁵ In experiments on fresh water algae a small amount of sodium bicarbonate was added to the water.

⁶ This acceleration is not due to the increase in the intensity of light as the sun gets higher for it was also observed when the experiments were started at noon.

⁷ When the sea water is not changed during the experiment the curve rises more rapidly at first then bends over to the right as the supply of CO₂ is used up.

⁸ This is because the catalyst from the moment of its production is in solution. It is not analogous to a solid going into solution, which dissolves more slowly as the limit of solubility is approached.

⁹ While respiration is in a sense the opposite of photosynthesis the steps in the process are apparently quite different from those found in photosynthesis.

¹⁰ I. e., under the conditions of the present experiment, where the reacting substances are kept approximately constant in composition.

¹¹ Aquatic plants taken directly from ice-covered ponds in winter are found to possess but feeble photosynthetic power, though of a deep green color.

¹² The activation of substances by light is well known in photochemistry.

¹³ *J. Biol. Chem., New York*, **21**, 1917, (585); **22**, 1917, (23).

MOBILITIES OF IONS IN AIR, HYDROGEN, AND NITROGEN

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Communicated by R. A. Millikan, January 21, 1918

In spite of the great number of investigations devoted to gases the question whether an ion is a molecule or an atom carrying an elementary charge, or whether it is a number of neutral molecules clustering about a charge is not as yet definitely settled. Both the 'cluster' hypothesis, according to which an ion is conceived of as a unit elementary charge surrounded by a satellite of neutral molecules, and the 'small-ion' hypothesis, according to which an ion is conceived of as a single molecule carrying an elementary charge, explain equally well the phenomenon which first necessitated the former, and also the older, hypothesis; this phenomenon being the fact that the mobilities and the diffusion coefficients of the ions in gases are relatively

small in comparison with those of the uncharged molecules in the same gases. They also explain equally well a certain number of other phenomena, but experiments designed to test directly the validity of one or the other of these hypotheses led to contradictory results.

The measurement of the mobilities of ions under various pressures and different electric field-strengths has always been generally conceded as the mode of attack in the solution of the problem. For if the older, the cluster, hypothesis is true the cluster would break up when the ion acquired a sufficiently high kinetic energy and the mobility would increase abnormally. But if the small-ion theory is true there would be no such dissociation and the mobility would remain normal. Quite a number of such measurements have been made, and they gave contradictory results. For instance, Latty,¹ Kovarik,² Todd,³ Townsend,⁴ Franck,⁵ Moore,⁶ Haines,⁷ and Ratner⁸ found the mobility to increase abnormally, whereas Chattock,⁹ Wellisch,^{10,11} and Loeb¹² found it normal over a wide range of potentials applied. In view of these results further experiments seemed desirable and hence the work herein described was undertaken.

The method here employed was the Rutherford¹³-Franck¹⁴ method as employed by Loeb.¹² The apparatus was fully described in Loeb's articles.

Results: a. Air.—An attempt first to repeat Loeb's work with air gave the following results:

TABLE 1
TABLE OF RESULTS OBTAINED FOR IONIC MOBILITIES IN AIR, FEBRUARY-MARCH, 1917

$U+$	$U-$	$X+$	$X-$	P	$K+$	$K-$	R
1. 60 cycles, 119 volts							
1.12	1.75	168	134	746	1.10	1.72	1.56
1.12	1.75	168	134	746	1.10	1.72	1.56
1.12	1.75	168	134	752	1.10	1.73	1.56
1.25	1.73	168	134	742	1.22	1.70	1.38
Mean.....					1.14	1.72	1.51
2. 14,758 cycles, 5000 volts							
1.64	1.98	14,160	12,870	752	1.62	1.92	1.21
1.57	1.84	14,160	12,870	750	1.56	1.82	1.17
1.64	1.98	14,160	12,870	749	1.61	1.95	1.21
1.57	1.84	14,160	12,870	746	1.55	1.81	1.17
1.82	2.10	13,810	12,650	692	1.66	1.92	1.17
2.26	2.61	12,300	11,550	558	1.66	1.91	1.16
Mean.....					1.61	1.90	1.18
Mean of both sets.....					1.37	1.81	1.34

$U+$ = Mobility of positive ions. $U-$ = Mobility of negative ions. X = Field strength in volt/cm. P = Pressure in mm. $R = K - /K$. K = Mobility at 760 mm. pres.

$X - /P$ Max. = 20.70, Min. = 0.18. $X + /P$ Max. = 22.04, Min. = 0.22.

It may be seen from the above table that the mean values of R , the ratio of the negative to the positive mobilities, are different for the two frequencies employed, and it appears as though the mobilities did vary—since the ratio could not vary unless either or both of the mobilities did. But the following considerations will show that this difference is ascribable to experimental variations. In the first place, the results of different experimenters, and even those of the same experimenter, show a maximum variation of almost 30%, for instance, from $R = 1.16$ to 1.37 (Wellisch), or from $R = 1.15$ to 1.93 (Loeb). Both of these authors attribute the variations to external variations of their experiments. Thus a slight external variation of some kind is liable to cause such a variation in the ratio without the mobilities themselves being varied at all. Furthermore, if the mobilities tend at all to vary with field-strength, their variations would be much greater than are manifested since the field-strength is 168 volt/cm. in one case and 14,160 volt/cm.

TABLE 2
RESULTS OBTAINED FROM THE MEASUREMENTS ON HYDROGEN, MAY-JUNE, 1917

$U+$	$U-$	$X+$	$X-$	P	$K+$	$K-$	R
<i>14,758 cycles, 4000 volts</i>							
5.51	8.20	6669	5668	748	5.43	8.10	1.49
5.92	8.20	6669	5668	748	5.81	8.10	1.38
5.51	8.20	6669	5668	746	5.40	8.10	1.49
8.20	12.21	5668	4723	518	5.58	8.35	1.49
14.94	20.99	4192	3524	290	5.70	8.15	1.41
14.94	20.99	4192	3524	300	5.84	8.35	1.41
Mean.....					5.56	8.19	1.45

in the other. Or, it may be said that even if the ratio does vary about 20% when the field-strength is increased from 169 to 14,160 volt/cm. (about 8333%), it may be considered constant for all practical purposes. However, there were enough of the experimental uncertainties to account for the variation.

Thus the conclusion is that between the field-strength of 168 and 14,160 volt/cm. the mobility of the positive ions remains absolutely normal, and the mobility of the negative ions remains normal also between 134 and 12,870 volt/cm.

These results more than amply substantiate those obtained by Loeb and it is therefore quite safe to conclude that the evidences obtained so far point decidedly in the direction of the small-ion theory.

b. Hydrogen. The results of the measurements in hydrogen with the high frequency high potential field are shown in table 2.

It may be seen from the table that with a potential gradient of 6669 volt/cm. or $X/p = 14.45$, the positive mobility remains normal. The nega-

tive mobility also remains absolutely normal with 5668 volt/cm. or $X/p = 12.15$. Thus it may be concluded that the law $Up = \text{constant}$, where $U = \text{mobility}$ and $p = \text{pressure in mm. mercury}$, is verified for hydrogen up to these limits.

Besides the normal positive and negative ions the existence of free negative electrons in hydrogen was proved. These electrons existed in abundance when the gas was freshly prepared and disappeared entirely after the gas had remained in the ionization chamber for about six or eight hours. The disappearance of the electrons might conceivably be the result either of their fast dissipation into the walls of the chamber or of their ready formation of negative ions with the neutral molecules of either hydrogen or the impurities from the sealing wax that had evaporated into the chamber in the meantime.

TABLE 3

$U+$	$U-$	$X+$	$X-$	P	$K+$	$K-$	R
<i>60 cycles</i>							
5.28		77.8		748	5.21		
5.50	8.80	25.0	16.5	746	5.41	8.65	1.52
6.60	11.19	20.0	13.0	600	5.22	8.80	1.62
8.95	13.28	29.5	24.0	498	5.85	8.70	1.48
13.90	22.00	19.8	11.5	300	5.49	8.69	1.58
22.91	31.06	16.5	99.0	198	5.95	8.15	1.34
	9.26		28.0	746		9.26	
Mean.....					5.52	8.71	1.57

$X - /P$ Max. = 12.15, Min. = 0.38. $X + /P$ Max. = 14.45, Min. = 0.66.

An effort was made to search for the two other kinds of negative ions which Haines claimed to have found.⁷ And as no trace of these other ions could be found it was thought that the disposition of the apparatus employed might not have been sufficiently adequate for their detection. Consequently it was considered desirable to repeat Haines' experiment in order to rectify the present method. Thus Haines' experimental conditions were reproduced as exactly as possible according to his descriptions with the expectation of obtaining similar results.

The results of this operation are shown in table 3.

These results agree with those obtained in the employment of the high frequency high potential field in showing that no such intermediate negative ions existed. This, together with a careful study of Haines' curves, led to the conclusion that in so far as experimental results are concerned there is not a scrap of evidence, either in Haines' results or in those obtained in the present experiment, of these other species of negative ions which were claimed to exist by Haines.

It may be proper to mention here that no sooner had the above conclusion been arrived at than it received corroboration from Wellisch's latest paper¹⁸ in which it was reported that no trace could be found of Haines' ions *B* and *C*.

Incidentally an interesting fact was revealed in the comparison between the two sets of curves. It was found that the amount of free negative electrons present in the gas was smaller when under high than when under low potential. This would seem to suggest that the electrons—or some of them at least—did actually attach themselves to neutral molecules when a high potential was applied and thus formed negative ions. This would not be at all

TABLE 4
RESULTS OBTAINED FOR NITROGEN, JULY, 1917

<i>U</i> +	<i>U</i> −	<i>X</i> +	<i>X</i> −	<i>P</i>	<i>K</i> +	<i>K</i> −	<i>R</i>
<i>1. 60 cycles</i>							
17.60	22.96	15.0	11.5	60	1.39	1.81	1.30
	10.15		26.0	140		1.87	
2.81	3.88	47.0	33.5	360	1.33	1.84	1.38
1.27	1.65	51.0	40.0	750	1.26	1.63	1.30
1.36	1.84	50.0	38.0	745	1.33	1.80	1.35
1.34	1.82	49.8	38.0	745	1.31	1.78	1.36
Mean.....					1.32	1.79	1.34
<i>2. 14,758 cycles, 5000 volts</i>							
1.31	1.84	17,670	14,880	750	1.29	1.82	1.40
1.31	1.84	17,670	14,880	745	1.28	1.80	1.40
1.31	1.84	17,670	14,880	742	1.28	1.80	1.40
2.76	3.93	13,910	10,110	360	1.31	1.86	1.42
2.76	3.93	13,910	10,110	345	1.26	1.78	1.42
Mean.....					1.28	1.81	1.41
Mean of both frequencies					1.30	1.80	1.38

$X - /P$ Max. = 29.0, Min. = 0.05. $X + /P$ Max. = 40.0, Min. = 0.07.

impossible since the tremendous velocity imparted to them by the high field would enable them to produce ions from neutral molecules by attaching themselves to the latter. It would be interesting to find out where, that is, at what potential—other conditions remaining the same—this sort of ionization actually would begin.

c. Nitrogen.—Table 4 shows the results of the mobility measurements in nitrogen. The maximum potential gradient employed was 17,670 volt/cm. for the positive and 14,880 volt/cm. for the negative ions. The mobilities remained absolutely normal up to these limits and the law $Up = \text{constant}$ was found to be applicable here as it was in the case of air and hydrogen.

Here too an abundance of free negative electrons was found, although the amount was not so great as that found in hydrogen under the same pressure.

Conclusion and Discussion.—As the results of the present experiment exhibit no deviation from the law $Up = \text{constant}$ it follows that both the positive and the negative ions did not disintegrate at the potentials employed. It may be seen from the tables that the values of X/p were very close to the values at which sparking would occur in the respective gases. And since the cluster hypothesis demands the disintegration of the ions when the values of X/p are much lower than those employed,¹⁵ it therefore follows that these results are directly contradictory to this hypothesis.

On the other hand, the results are in perfect accord with the small-ion hypothesis. Taking this in conjunction with the results of other experiments, especially those of Wellisch and Loeb, there does not seem any question at all regarding the validity of this hypothesis.

There remains, however, an experimental fact which the cluster hypothesis seems to be able to explain better than the small-ion hypothesis, and that is the difference between the mobilities of the positive and the negative ions. For, if both the positive and the negative ions are single molecules carrying elementary charges different only in signs, why should they have different mobilities? Whereas if the ions are clusters the difference in their mobilities may be ascribed to the difference between the numbers of molecules constituting the two kinds of ions.

This difficulty of the small-ion theory, however, is more apparent than real in view of the recent theories as to the electronic constitution of matter. If an atom consists of a positive nucleus surrounded by a satellite of negative electrons held together by the attractive force from the nucleus, the phenomenon of ordinary molecular collision must be attributed to the repulsion between the two systems of negative electrons in the colliding molecules^{16, 17}. Since, according to the small-ion theory, the only difference between the uncharged molecules and the ions lies in the number of negative electrons in the satellites—the negative ion having one more electron, and the positive ion one less than the uncharged molecules—it follows that the only difference between the ordinary molecular collisions and the collisions between ions and uncharged molecules is that between the numbers of electrons in the colliding systems. It is only reasonable, therefore, to extend the conception of the ordinary molecular collision to cover the case of collision between ions and uncharged molecules. Now since the negative ion has more of these peripheral negative electrons than the positive ion it follows that the repulsion between the negative ion and the uncharged molecule is greater than that between the positive ion and the uncharged molecule; and the attractive force between the negative ion and the uncharged molecule is smaller than that between the positive ion and the uncharged molecule. This results in a difference in the *effective mean free paths* of the two kinds of ions. The positive ion, by virtue of the greater attractive force existing between it and the uncharged

molecules, drags the latter more towards it and thus has a smaller *effective mean free path*. The negative ion, with the smaller attractive force, has a greater *effective mean free path*. As the mobility varies directly with the mean free path, it can be easily seen why the negative ions have a greater mobility than the positive ions.

But the above explanation would not be applicable to the case where the ratio of the negative to the positive mobility is less than unity, for that would mean that the attractive force between the negative and the uncharged molecule is greater than that between the positive ion and the uncharged molecule, which would be impossible according to the theory upon which the explanation is based. Fortunately, in such cases the differences between the positive and the negative mobilities are so small that they are well within the limits of experimental fluctuations; consequently, until it is conclusively established that there are cases where the positive mobilities are greater than the negative by a quantity much too great to be accounted for by experimental conditions, the above explanation seems to be the most reasonable one so far advanced.

The detailed paper has been communicated to the *Physical Review*.

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⁵ Franck, J., *Ann. Physik, Leipzig*, **22**, 1906, (972).

⁶ Moore, *Physic. Rev., Ithaca, N. Y.*, 1912.

⁷ Haines, *Phil. Mag., London*, **30**, 1915; **31**, 1916.

⁸ Ratner, *Ibid.*, **32**, 1916.

⁹ Chattock, *Ibid.*, **48**, 1899, (401).

¹⁰ Wellisch, *London, Phil. Trans. R. Soc.*, (A), **209**, 1909.

¹¹ Wellisch, *Amer. J. Sci., New Haven*, May, 1915; *Phil. Mag., London*, March, 1916.

¹² Loeb, *Physic. Rev., Ithaca, N. Y.*, **8**, 1916, (633); these PROCEEDINGS, **2**, 1916, (633).

¹³ Rutherford, *Cambridge, Proc. Phil. Soc.*, **9**, 1898, (410).

¹⁴ Franck, *Ann. Physik, Leipzig*, **21**, 1906, (985).

¹⁵ Townsend, *Electricity in Gases*, Oxford, 1915.

¹⁶ Rutherford, *Phil. Mag., London*, **21**, 1911, (669).

¹⁷ Millikan, *The Electron*, Chicago, 1917.

¹⁸ Wellisch, *Phil. Mag., London*, **32**, 1917, (199).